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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE MAY 08 2001

ANDREAS WINTER ET AL

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REISSUE APPLICATION OF US PATENT 5,693,836 : EXAMINER: N. GONZALEZ

SERIAL NUMBER: 09/488,037

: ART UNIT: 1621

FILING DATE: JANUARY 19, 2000

:

ISSUED: DECEMBER 2, 1997

:

FOR: PROCESS FOR THE PREPARATION OF
POLYOLEFINS

:BOX AF

Asst. Commissioner for Patents And Trademarks

Washington, D.C. 20231

I HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS
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WASHINGTON D.C. 20231 ON THIS 30th DAY OF April 2001 BY: Camie A. McPherson

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APPEAL BRIEF

I. THE REAL PARTY OF INTEREST

Basell Propylene is the real party in interest. Targor GmbH has recently changed its
name to Basell Propylene.

II. RELATED APPEALS AND INTERFERENCES

The undersigned is aware of a pending appeal that may be material (Serial No.
09/365,624). The Appeal Brief for Serial N.. 09/365,624 was recently filed. Although the
claims of these applications do not overlap, copending serial no. 09/365,624 and the original
issued claims from US 5,693,836 (" '836 patent") (this application is the reissue application of

the '836 patent) were both involved in separate interferences involving the Karl application which eventually became US Patent 6,096,912 (see Exhibit A). The '836 patent was involved in an interference no. 104,447 in which issued claims 1-3 of the '836 patent were lost.

III. THE STATUS OF THE CLAIMS

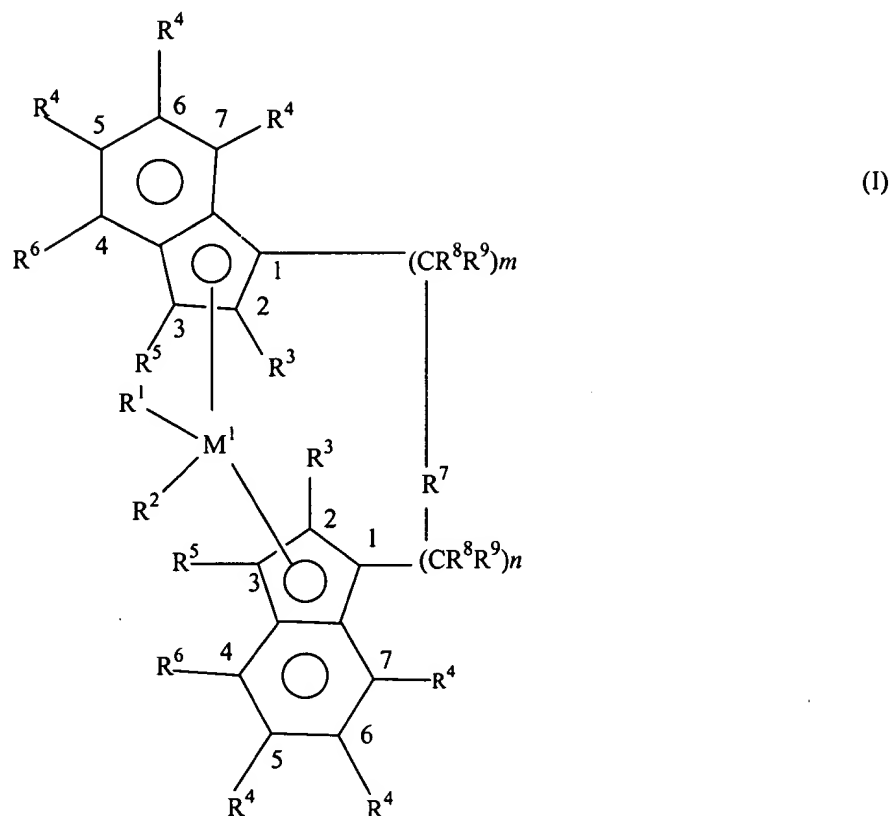
Claims 1-3 have been rejected and are the subject of this appeal. These claims are attached in Appendix I with all the changes incorporated therein. Appendix II lists the reissue claims without the amendments being incorporated therein. All the changes are listed with the terms added being underlined and the terms deleted being bracketed.

IV. STATUS OF AMENDMENTS AFTER FINAL

A Request for Reconsideration was filed January 18, 2001 and was made of record pursuant to the Advisory Action mailed February 5, 2001 (Paper No. 8). An Amendment After was mailed February 26, 2001 and was entered and made of record pursuant to the Advisory Action mailed March 9, 2001 (Paper No. 10).

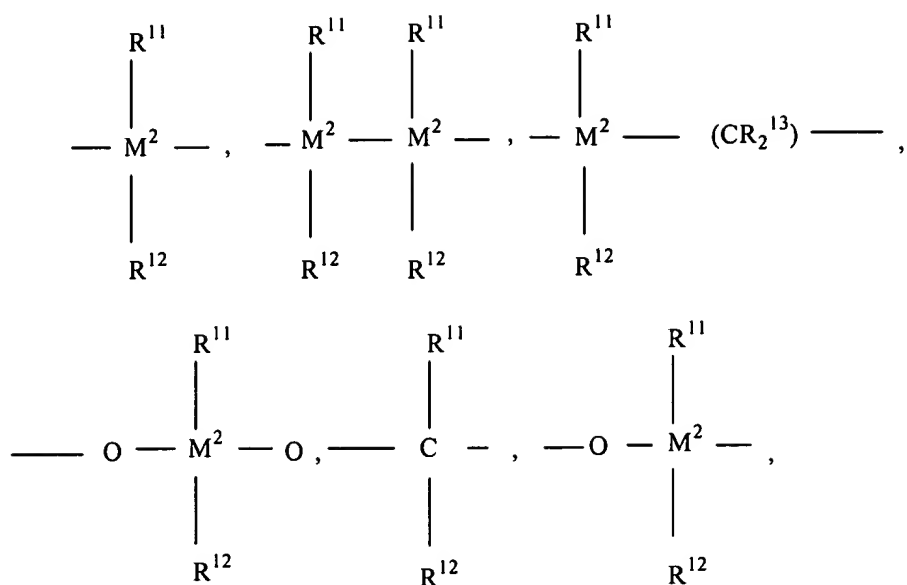
V. SUMMARY OF THE INVENTION

1. A compound of the formula I in its pure meso-form or as a meso:rac > 1:99 mixture,



in which M^1 , R^1 , R^2 and the radicals R^4 and R^5 are defined in claim 1, R^3 and R^6 are not hydrogen,

R^7 (the bridge between the two indenyl ligands) is



wherein

R¹¹ and R¹² are different and are defined in claim 1 and

R¹³, M², R⁸ and R⁹, m and n are defined in claim 1.

The numbering of 1-7 on the ring system (ligand) indicates the position that is substituted. For example, since R³ and R⁶ are not hydrogen, the 2 and 4 positions of each of the ligands must be substituted.

The application contains three claims and two independent claims (claims 1 and 3). All three claims have been narrowed since the Decision of the Board in the interference. With respect to claim 1, the applicants have deleted the possibility of forming a benzindenyl ring as is required by the Karl application which again matured into US Patent 6,096,912 (see Exhibit A).

In addition, the applicants' claimed invention not only excludes the benzoindenyl ligand, but also excludes the possibility that the bridge R⁷ has identical substituents R¹¹ and R¹².

The other independent claim is claim 3 which is directed to four specific metallocene compounds that are $\text{Me}_2\text{Si}(2,4,6\text{-trimethyl-1-indenyl})_2\text{ZrCl}_2$, $\text{Me}_2\text{Si}(2\text{-methyl-4,6-diisopropyl-1-indenyl})_2\text{ZrCl}_2$, $\text{Me}_2\text{Si}(2\text{-methyl-4-phenyl-1-indenyl})_2\text{ZrCl}_2$ or ethylene(2,4,6-trimethyl-1-indenyl) $_2\text{ZrCl}_2$. Again, the ring system claim is only an indenyl ligand system.

VI. REFERENCE APPLIED AGAINST THE CLAIMS

There are no references applied against the claims.

VII. THE REJECTION APPEALED FROM

1. Claims 1-3 were rejected under Interference Estoppel.

VIII. THE ISSUES ON APPEAL

1. Whether claims 1-3 are rejectable under Interference Estoppel?
2. Whether Group I is patentably distinct from the count?
3. Whether Group II is patentably distinct from the count?
4. Whether *ex parte* Deckler should be used as a precedent in this application?

IX. GROUPING OF THE CLAIMS

Claims 1-3 are pending in this case. These claims do not stand or fall together.

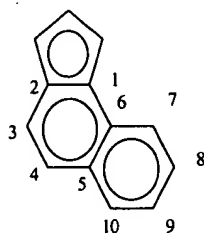
Group I hereinafter refers to claims 1 and 2.

Group II hereinafter refers to claim 3.

X. ARGUMENTS

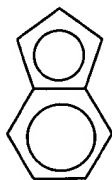
A. Group I

Claim 1 has been amended since the interference. The applicants have deleted the possibility of forming a benzindenyl ligand as is required by the Karl application. A benzindenyl ligand is as follows:



The benzindenyl ligand has the two benzene rings attached to the cyclopentadienyl ligand. There are an additional ten carbon atoms present (see the numbers 1-10) being bonded to the cyclopentadienyl ligand. Claim 1 of Karl requires that R^3 and R^4 and R^5 and R^6 in each case together form, a hydrocarbon ring system of 10 to 15 carbon atoms. The benzindenyl ligand has the minimum of 10 carbon atoms. This is the minimum ring system claimed in Karl.

The applicants' claim 1 is limited to an indenyl ligand:



The indenyl ligand only contains 6 carbon atom (benzene ring) bonded to the cyclopentadienyl ring.

The Karl patent requires another ring being formed to the indenyl ligand. The applicants have amended the claim 1 to exclude the possibility of having another ring formed with the indenyl ligand. The applicants have deleted the possibility that "two or more radicals R^2 - R^6 , together with the atoms connecting them, form a ring system".

In addition to not containing the ring system of Karl, the applicants' claimed invention also excludes the possibility that the bridge R^7 has identical substituents (R^{11} and R^{12}). In the applicants' application, the substituents R^{11} and R^{12} are different and they are not identical as is required by Karl. Karl's substituents in the bridge are "Z". Z is not disclosed nor claimed as being different.

Claims 1-3 were rejected on the basis of interference estoppel under 37 CFR §1.658(c). The applicants believe that the claimed subject matter is patentably distinct over the Count. The applicants have deleted the possibility of having a 4,5-benzindenyl ligands from their claimed invention. In the Advisory Action, the Examiner correctly referred to the Count as being claim 1 of the Winter patent or claim 1 of the Karl application. It is true that claim 1 has been amended by not only changing the substituents to being different, but also limited the possibility that the substituents in the indenyl ring form a further ring (see Appendix II). The applicants however are claiming a much narrower invention than originally claimed.

In the Final Office Action dated November 1, 2000, and the Advisory Action dated March 9, 2001, the Examiner has cited *In re Kroekel, et al.*, 231 U.S.P.Q. 640 (CAFC 1986) as authority to prevent Applicants from presenting the present claims in *ex parte* proceedings. In *Kroekel*, the

Court denied applicants' argument that they had no obligation to broaden the lost claim during the interference proceeding, but could show via Rule 1.131 affidavits that they were the first inventors of the generic invention. The Applicants respectfully disagree with the Examiner's assertion that *In re Kroekel* is applicable.

In *Kroekel*, the applicants were attempting to broaden claims. In the prior interference, only the "species" that was common to both applications was adjudicated. *Kroekel* did not attempt to include the genus in the interference. The amended claim he presented after the interference did "not exclude the precise subject matter lost in the interference." *Kroekel* at 644. The Court stated "[i]f [a] claim [is] patentably distinct from the lost count, it [can] not be denied to [Applicants] on the sole ground of interference estoppel." *Id.* at 643 (citation omitted). In the present application, the Applicants are narrowing the claims so as to exclude the precise subject matter lost in the interference and to be patentably distinct from the Count of the interference. The applicants are not trying to broaden their claims, but instead narrow their claims. The CAFC stated that a second interference would have to be declared if they permitted the broadening of the claims. However, in the applicants' situation a second interference would not be declared, since there is clearly no overlap in the applicants' claimed invention and the disclosure or claims of Karl. For the above reasons, the applicants do not believe that *In re Koekel* is related to the Applicants' situation.

During the interview conducted July 7, 2000, the Examiner stated that interference estoppel would apply and referred to *Ex parte Tytgat*, 225 U.S.P.Q. 907 (Bd. App. 1985). In this case, the Board did not believe that the difference (in the claimed invention) renders the subject matter on appeal patentably distinct from the subject matter of the "lost" counts. *Ex parte Tytgat, supra* at

page 910.

Furthermore, the Board stated,

“Thus, it is our view that if a patent is issued to Tytgat containing the claims on appeal, **two patents claiming patentably indistinct inventions will have been issued.**” *Tytgat, supra* at page 910. (Emphasis added)

This is clearly not the applicants’ situation since there is no overlap between the applicants’ claimed invention and Karl’s claimed application (the application involved in the interference). The two patents are not claiming the same invention. Karl’s application does not disclose nor claim that the substituents in the bridges are different and that the metallocene is limited to indenyl ligands. The applicants’ claimed invention requires that the substituents are different and are only indenyl ligands.

The Board further emphasized at page 911,

“We think it most unlikely that Congress could have intended for **two patents to be issued to different parties for a single inventive concept.**” Emphasis added

Clearly there is not a single inventive concept when both patents can issue without any overlapping subject matter as is in this case.

The applicants believe that a more recent decision *Ex parte Deckler* 21 U.S.P.Q.2d 1872 (Bd. App. 1991) is applicable. In this case, the Board of Appeals stated that interference estoppel is proper with respect to claims that contain subject matter identical to both applications and relied upon *Ex parte Tytgat, supra*. However, the Board in this case reversed the rejections of interference estoppel inasmuch as the claims do not read directly on common disclosure of the losing and winning parties and cited *In re Risse*, 378 F.2d 948, 154 U.S.P.Q. 1 (C.C.P.A. 1967) and *In re*

Wilding, 535 F.2d 631, 190 U.S.P.Q. 59 (C.C.P.A. 1976). (See *Ex parte Deckler*, *supra* at page 1874). As stated above, (1) Karl does not have any disclosure that states that the substituents on the bridge can be different. (2) Karl does not claim indenyl ligands (see claim 1 of Karl, R³ and R⁴ and R⁵ and R⁶ in each case together form, a hydrocarbon ring system of 10 to 15 carbon atoms). A cyclopentadienyl ring system containing a six carbon atom ring would be an indenyl ligand system. A cyclopentadienyl ring system 10 carbon atoms ring system would be a benzindenyl ligand system as described above. For the above reasons the applicants respectfully request that this rejection be withdrawn.

B. Group II

This group of claims is limited to four specific species, all limited to substituted indenyl ligands requiring at least two specific substituents at specific locations on the indenyl ligand. These species are not at all disclosed in the Karl application. The applicants believe that there is no suggestion or teaching in the Karl application to cover these species. It is noted that the original claim 3 had thirteen species and was designated as corresponding to the count. However, the applicants have deleted nine of the thirteen species and believe that these are patentable distinct from the count and the original claim 3.

Furthermore, the only four remaining examples are not disclosed nor claimed by Karl. Me₂Si(2,4,6-trimethyl-1-indenyl)₂ZrCl₂ corresponds to examples 7 and 19 in the specification. Me₂Si(2-methyl-4,6-diisopropyl-1-indenyl)₂ZrCl₂ corresponds to example 8 in the specification. Me₂Si(2-methyl-4-phenyl-1-indenyl)₂ZrCl₂ corresponds to examples 11, 21 and 34 in the specification. Ethylene(2,4,6-trimethyl-1-indenyl)₂ZrCl₂ corresponds to example 13 in the

specification. The applicants have shown comparative examples in Table 6 of the specification.

As stated above, the applicants believe that *Ex parte Deckler supra* should apply. As stated above, (1) Karl does not disclose nor claim the applicants' specifically claimed metallocene indenyl compounds (see claim 1 of Karl, R³ and R⁴ and R⁵ and R⁶ in each case together form, a hydrocarbon ring system of 10 to 15 carbon atoms). A cyclopentadienyl ring system containing six additional carbon atoms would be an indenyl ligand system. A cyclopentadienyl ring system containing an additional 10 carbon atoms would be a benzindenyl ligand system.. This group is limited to four specific metallocene species all containing specifically substituted indenyl ligands. These are not disclosed nor taught by Karl. Since there is no overlap with Karl, the applicants respectfully request that this rejection be withdrawn.

XI. CONCLUSION

It is believed that the claims define an invention which is new, useful, and unobvious. If the applicants are awarded priority in the interference, the applicants request passage to allowance. This brief is being submitted in triplicate along with a check in the amount of \$310.00.

However, in the event that the undersigned is mistaken in his calculations, an appropriate extension of time to respond is respectfully petitioned for, and the Commissioner is hereby authorized to charge the account of the undersigned attorneys, Patent Office Deposit Account No. 03-2775, for any fees which may be due upon the filing of this paper.

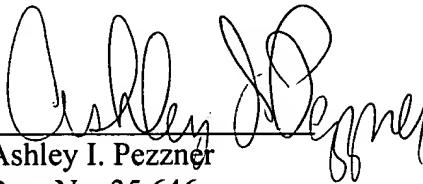
SERIAL NUMBER: 09/488,037

92/F 253 (5591*404)

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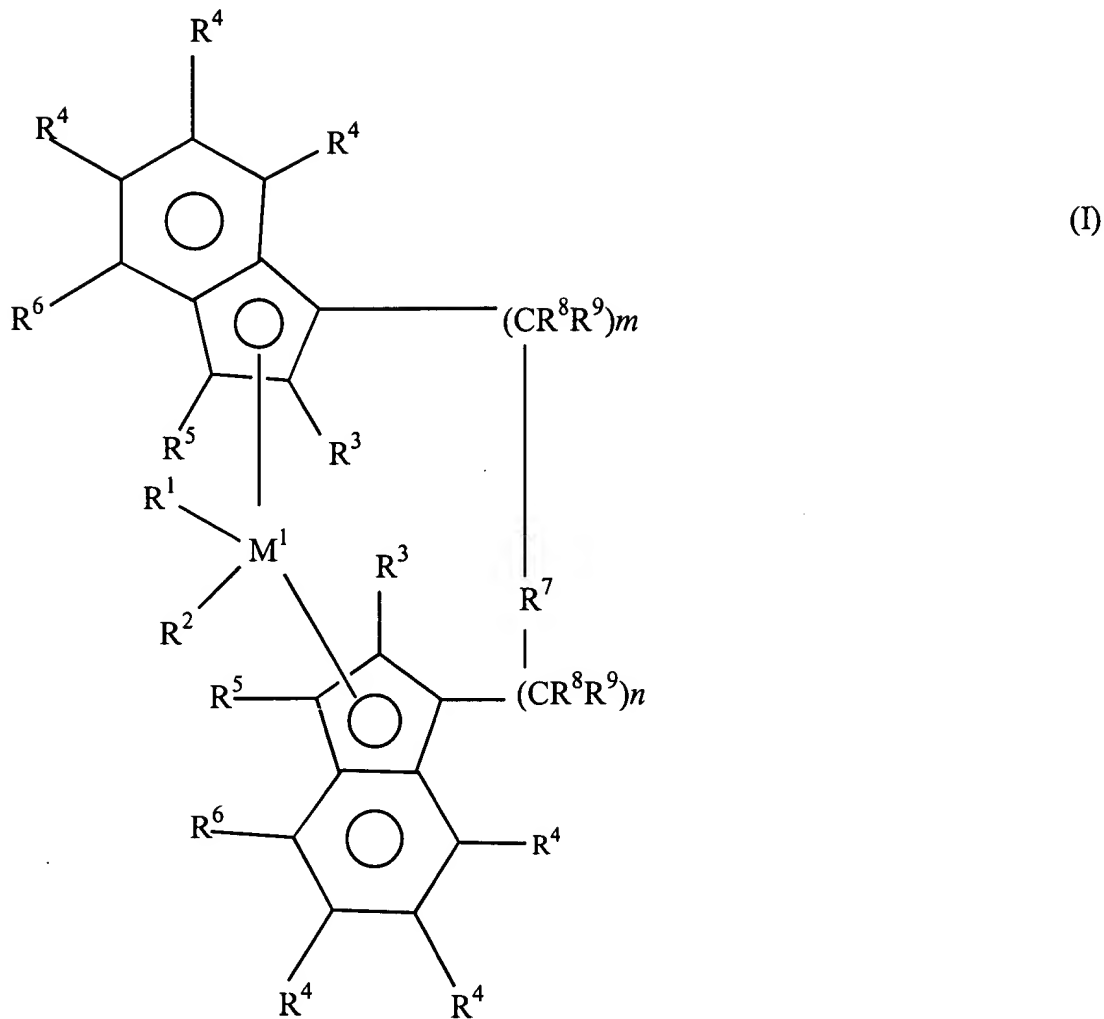
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APPENDIX I

1. A compound of the formula I in its pure meso-form or as a meso:rac > 1:99 mixture,



in which

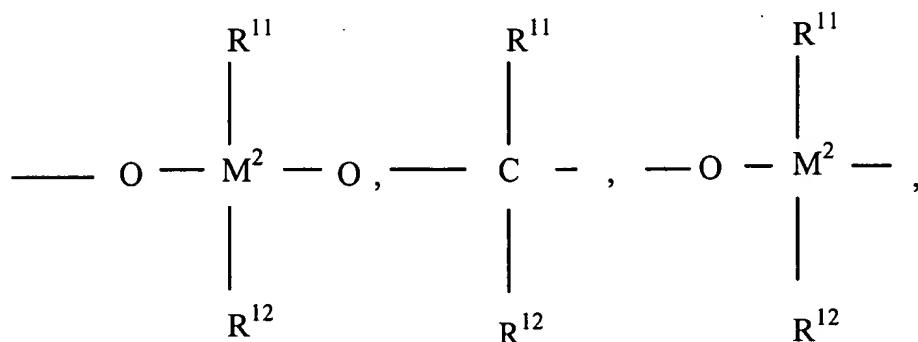
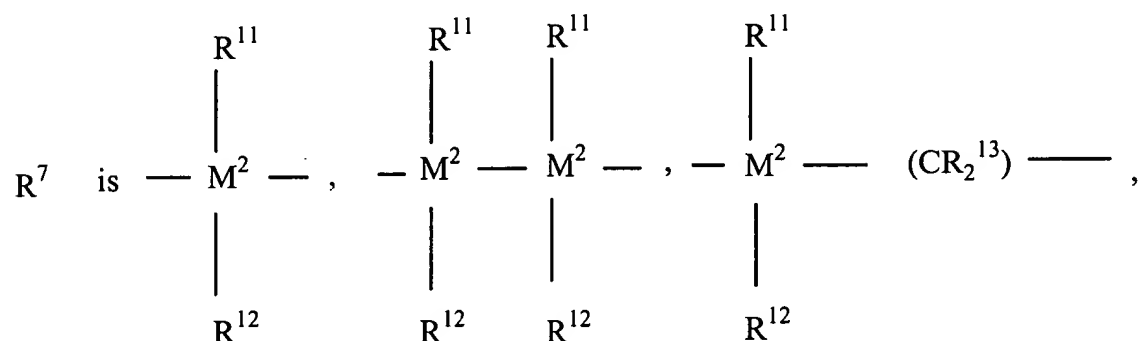
M^1 is a metal from group IVb, Vb or VIb of the Periodic Table,

R^1 and R^2 are identical or different and are a hydrogen atom, a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -alkoxy group, a C_6 - C_{10} -aryl group, a C_6 - C_{10} -aryloxy group, a C_2 - C_{10} -alkenyl group, a C_7 - C_{40} -arylalkyl group, a C_7 - C_{40} -alkylaryl group, a C_8 - C_{40} -arylalkenyl group or a halogen atom,

the radicals R^4 and R^5 are identical or different and are a hydrogen atom, a halogen atom, a C_1 - C_{10} -alkyl group, which may be halogenated, a C_6 - C_{10} -aryl group, which may be halogenated, or an $-NR_2^{10}$, $-SR^{10}$, $-OSiR_3^{10}$, $-SiR_3^{10}$ or $-PR_2^{10}$

radical in which R^{10} is a halogen atom, a C_1 - C_{10} -alkyl group or a C_6 - C_{10} -aryl group,

R^3 and R^6 are identical or different and are as defined for R^4 , with the proviso that R^3 and R^6 are not hydrogen,



where

R^{11} and R^{12} are different and are a hydrogen atom, a halogen atom, a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -fluoroalkyl group, a C_6 - C_{10} -aryl group, a C_6 - C_{10} -fluoroaryl group, a C_1 - C_{10} -alkoxy group, a C_2 - C_{10} -

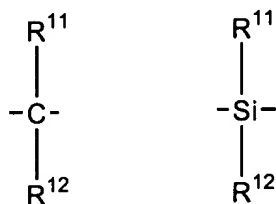
alkenyl group, a C₇-C₄₀-arylalkyl group, a C₈-C₄₀-arylalkenyl group or a C₇-C₄₀-alkylaryl group, R¹³ is a hydrogen atom, a halogen atom, a C₁-C₁₀-alkyl group, a C₁-C₁₀-fluoroalkyl group, a C₆-C₁₀-aryl group, a C₆-C₁₀-fluoroaryl group, a C₁-C₁₀-alkoxy group, a C₂-C₁₀-alkenyl group, a C₇-C₄₀-arylalkyl group, a C₈-C₄₀-arylalkenyl group or a C₇-C₄₀-alkylaryl group,

or R¹¹ and R¹², or R¹¹ and R¹³, in each case together with the atoms connecting them, form a ring, M² is silicon, germanium or tin,

R⁸ and R⁹ are identical or different and are as defined for R¹¹, and

m and n are identical or different and are zero, 1 or 2, where m plus n is zero, 1 or 2.

2. A compound as claimed in claim 1, wherein, in the formula I, M¹ is Zr or Hf, R¹ and R² are identical or different and are methyl or chlorine, R³ and R⁶ are identical or different and are methyl, isopropyl, phenyl, ethyl or trifluoromethyl, R⁴ and R⁵ are hydrogen or as defined for R³ and R⁶, R⁷ is a

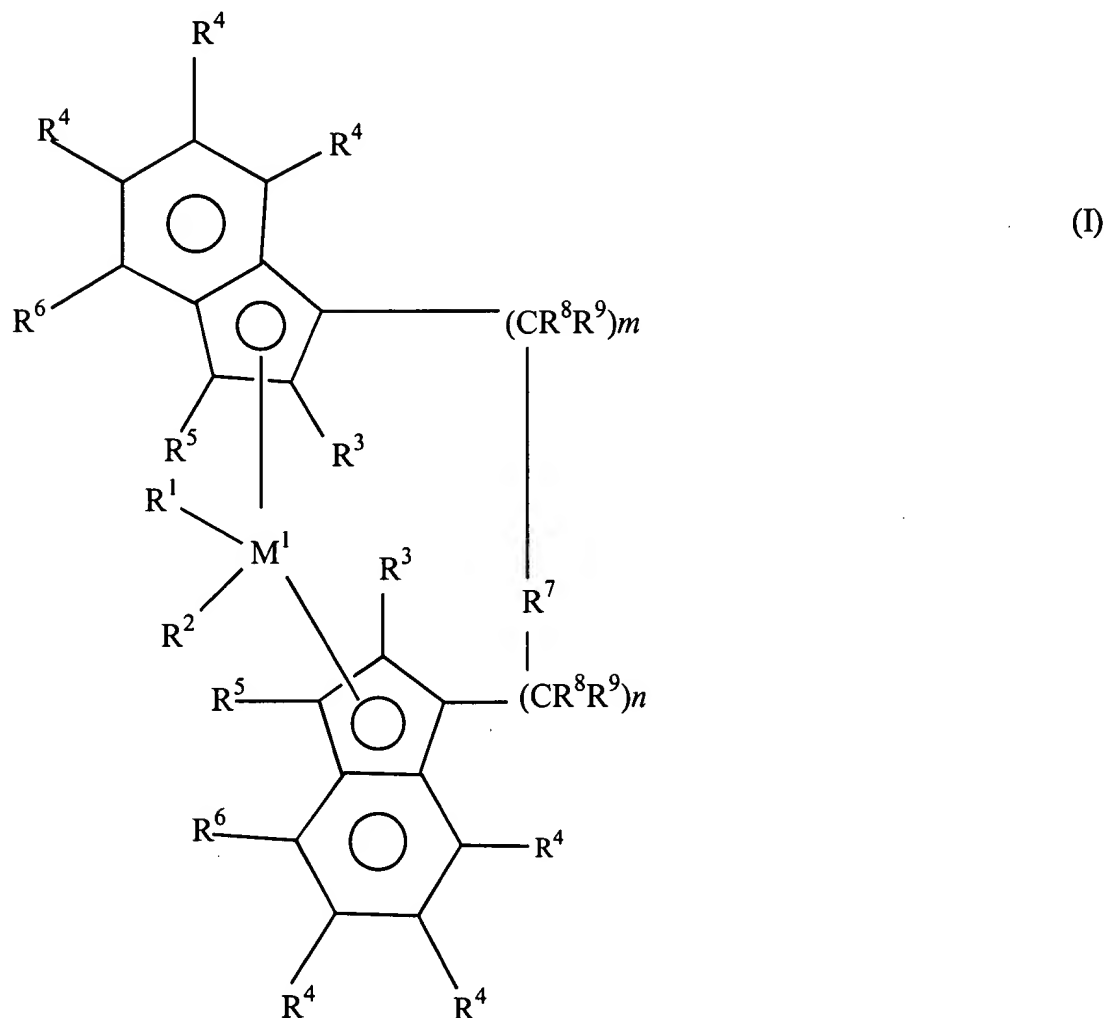


radical, and m plus n are zero or 1.

3. A compound selected from the group consisting of Me₂Si(2,4,6-trimethyl-1-indenyl)₂ZrCl₂, Me₂Si(2-methyl-4,6-diisopropyl-1-indenyl)₂ZrCl₂, or Me₂Si(2-methyl-4-phenyl-1-indenyl)₂ZrCl₂, ethylene(2,4,6-trimethyl-1-indenyl)₂ZrCl₂.

APPENDIX II

1. A compound of the formula I in its pure meso-form or as a meso:rac > 1:99 mixture,



in which

M^1 is a metal from group IVb, Vb or VIb of the Periodic Table,

R^1 and R^2 are identical or different and are a hydrogen atom, a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -alkoxy group, a C_6 - C_{10} -aryl group, a C_6 - C_{10} -aryloxy group, a C_2 - C_{10} -alkenyl group, a C_7 - C_{40} -

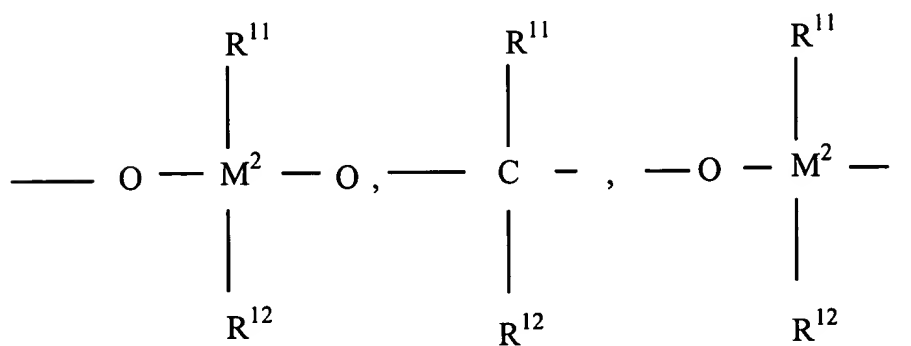
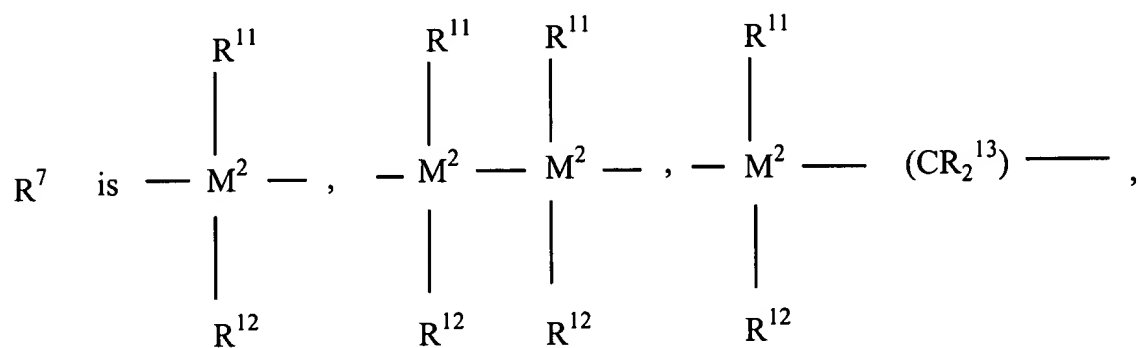
arylalkyl group, a C₇-C₄₀-alkylaryl group, a C₈-C₄₀-arylalkenyl group or a halogen atom,

the radicals R⁴ and R⁵ are identical or different and are a hydrogen atom, a halogen atom, a C₁-C₁₀-alkyl group, which may be halogenated, a C₆-C₁₀-aryl group, which may be halogenated, or an -NR₂¹⁰, -SR¹⁰, -OSiR₃¹⁰, -SiR₃¹⁰ or -PR₂¹⁰

radical in which R¹⁰ is a halogen atom, a C₁-C₁₀-alkyl group or a C₆-C₁₀-aryl group,

R³ and R⁶ are identical or different and are as defined for R⁴, with the proviso that R³ and R⁶ are not hydrogen,

[or two or more of the radicals R³ to R⁶, together with the atoms connecting them, form a ring system,]



[>BR¹¹, >AIR¹¹, -Ge-, -Sn-, -O-, -S-, >SO, >SO₂, >NR¹¹, >CO, >PR¹¹ or >P(O)R¹¹,]

where

R^{11} , R^{12} and R^{13} are identical or] and R^{12} are different and are a hydrogen atom, a halogen atom, a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -fluoroalkyl group, a C_6 - C_{10} -aryl group, a C_6 - C_{10} -fluoroaryl group, a C_1 - C_{10} -alkoxy group, a C_2 - C_{10} -alkenyl group, a C_7 - C_{40} -arylalkyl group, a C_8 - C_{40} -arylalkenyl group or a C_7 - C_{40} -alkylaryl group,

R^{13} is a hydrogen atom, a halogen atom, a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -fluoroalkyl group, a C_6 - C_{10} -aryl group, a C_6 - C_{10} -fluoroaryl group, a C_1 - C_{10} -alkoxy group, a C_2 - C_{10} -alkenyl group, a C_7 - C_{40} -arylalkyl group, a C_8 - C_{40} -arylalkenyl group or a C_7 - C_{40} -alkylaryl group,

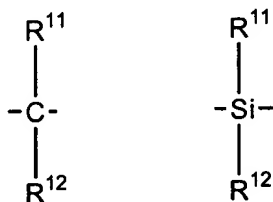
or R^{11} and R^{12} , or R^{11} and R^{13} , in each case together with the atoms connecting them, form a ring,

M^2 is silicon, germanium or tin,

R^8 and R^9 are identical or different and are as defined for R^{11} , and

m and n are identical or different and are zero, 1 or 2, where m plus n is zero, 1 or 2.

2. A compound as claimed in claim 1, wherein, in the formula I, M^1 is Zr or Hf, R^1 and R^2 are identical or different and are methyl or chlorine, R^3 and R^6 are identical or different and are methyl, isopropyl, phenyl, ethyl or trifluoromethyl, R^4 and R^5 are hydrogen or as defined for R^3 and R^6 , [or R^4 forms an aliphatic or aromatic ring with R^6 , or adjacent radicals R^4 form an aliphatic or aromatic ring, and] R^7 is a



radical, and m plus n are zero or 1.

3. A compound [as claimed in claim 1, wherein the compound of the formula I is] selected from the group consisting of $[\text{Me}_2\text{Si}(2,4\text{-dimethyl-1-indenyl})_2\text{ZrCl}_2, \text{Me}_2\text{Si}(2\text{-methyl-4-isopropyl-1-indenyl})_2\text{ZrCl}_2, \text{Me}_2\text{Si}(2\text{-ethyl-4,methyl-1-indenyl})_2\text{ZrCl}_2, \text{Ph}(\text{Me})\text{Si}(2\text{-methyl-4-isopropyl-1-indenyl})_2\text{ZrCl}_2, \text{Me}_2\text{Si}(2\text{-methyl-4,5-benzoindenyl})_2\text{ZrCl}_2,] \text{Me}_2\text{Si}(2,4,6\text{-trimethyl-1-indenyl})_2\text{ZrCl}_2, \text{Me}_2\text{Si}(2\text{-methyl-4,6-diisopropyl-1-indenyl})_2\text{ZrCl}_2, [\text{Me}_2\text{Si}(2\text{-methyl-}\alpha\text{-acenaphth-indenyl})_2\text{ZrCl}_2,]$ or $\text{Me}_2\text{Si}(2\text{-methyl-4-phenyl-1-indenyl})_2\text{ZrCl}_2, \text{ethylene}(2,4,6\text{-trimethyl-1-indenyl})_2\text{ZrCl}_2, [\text{ethylene}(2\text{-methyl-4,5-benzoindenyl})_2\text{ZrCl}_2, \text{methylethylene}(2\text{-methyl-}\alpha\text{-acenaphthindenyl})_2\text{ZrCl}_2$ or $\text{Ph}(\text{Me})\text{Si}(2\text{-methyl-}\alpha\text{-acenaphthindenyl})_2\text{ZrCl}_2]$.

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EXhibit A



US006096912A

United States Patent [19]

Karl et al.

[11] **Patent Number:** **6,096,912**[45] **Date of Patent:** ***Aug. 1, 2000****[54] SOLUBLE CATALYST SYSTEMS FOR THE PREPARATION OF POLYALK-1-ENES HAVING HIGH MOLECULAR WEIGHTS**

[75] **Inventors:** Eberhard Karl; Werner Roell, both of Constance; Hans Brintzinger, Leimbach-Guntershausen; Bernhard Rieger, Nehren; Udo Stehling, Constance, all of Germany

[73] **Assignee:** BASF Aktiengesellschaft, Ludwigshafen, Germany

[*] **Notice:** Under 35 U.S.C. 154(b), the term of this patent shall be extended for 381 days.

[21] **Appl. No.:** 08/642,491

[22] **Filed:** May 3, 1996

Related U.S. Application Data

[62] Division of application No. 08/375,278, Jan. 19, 1995, Pat. No. 5,514,760, which is a continuation of application No. 08/158,777, Dec. 1, 1993, abandoned, which is a division of application No. 07/900,427, Jun. 18, 1992, Pat. No. 5,296,434.

[30] Foreign Application Priority Data

Jun. 18, 1991 [DE] Germany 41 20 009

[51] **Int. Cl.⁷** **C07F 17/00**

[52] **U.S. Cl.** **556/11; 556/12; 556/22; 556/23; 556/43; 556/53; 526/127; 526/160; 526/351; 526/943; 502/103; 502/117; 502/155; 502/158**

[58] **Field of Search** **556/11, 12, 22, 556/23, 43, 53; 526/127, 160, 351, 943; 502/103, 117, 155, 158**

[56] References Cited**U.S. PATENT DOCUMENTS**

4,794,096 12/1988 Ewen 502/117

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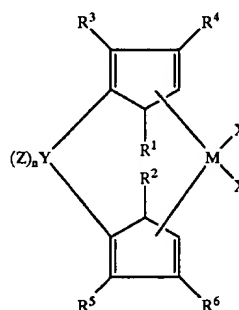
0 185 918 A2 7/1986 European Pat. Off. .
0 283 739 A2 9/1988 European Pat. Off. .
0 284 708 A1 10/1988 European Pat. Off. .
0 316 155 B1 5/1989 European Pat. Off. .
0 355 447 A2 2/1990 European Pat. Off. .
2 207 136 1/1989 United Kingdom .

Primary Examiner—Porfirio Nazario-Gonzalez
Attorney, Agent, or Firm—Keil & Weinkauff

[57] ABSTRACT

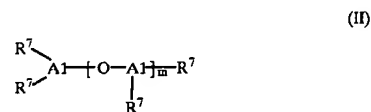
Abstract of the Disclosure: Catalyst systems for the polymerization of C₂-C₁₀-alk-1-enes contain, as active components,

a) a metallocene complex of the general formula I



where M is titanium, zirconium, hafnium, vanadium, niobium or tantalum, X is halogen or C₁-C₈-alkyl, Y is carbon, phosphorus, sulfur, silicon or germanium, Z is C₁-C₈-alkyl, C₃-C₁₀-cycloalkyl or C₆-C₁₀-aryl, R¹ and R² are identical or different and are each C₁-C₄-alkyl, R³ to R⁶ are identical or different and are each hydrogen or C₁-C₈-alkyl, or two adjacent radicals R³ and R⁴ and R⁵ and R⁶ in each case together form a hydrocarbon ring system of 4 to 15 carbon atoms and n is 0, 1 or 2, and

b) an open-chain or cyclic alumoxane compound of the general formula II or III



where R⁷ is C₁-C₄-alkyl and n is from 5 to 30.

The novel catalyst systems are particularly suitable for the preparation of polyalk-1-enes having high molecular weights.

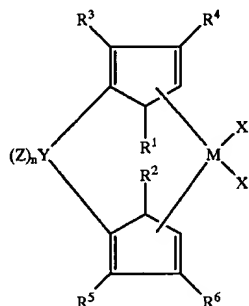
7 Claims, No Drawings

SOLUBLE CATALYST SYSTEMS FOR THE PREPARATION OF POLYALK-1-ENES HAVING HIGH MOLECULAR WEIGHTS

This is a division of application Ser. No. 08/375,278, filed Jan. 19, 1995, now U.S. Pat. No. 5,514,760, which is a FWC of Ser. No. 08/158,777, filed on Dec. 1, 1993, now abandoned, which is a division of Ser. No. 07/900,427, filed Jun. 18, 1992 now U.S. Pat. No. 5,296,434.

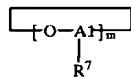
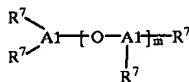
The present invention relates to catalyst systems for the polymerization of C_2 - C_{10} -alk-1-enes, containing, as active components,

a) a metallocene complex of the general formula I



where M is titanium, zirconium, hafnium, vanadium, niobium or tantalum, X is halogen or C_1 - C_8 -alkyl, Y is carbon, phosphorus, sulfur, silicon or germanium, Z is C_1 - C_8 -alkyl, C_3 - C_{10} -cycloalkyl or C_8 - C_{10} -aryl, R^1 and R^2 are identical or different and are each C_1 - C_4 -alkyl, R^3 to R^6 are identical or different and are each hydrogen or C_1 - C_8 -alkyl, or two adjacent radicals R^3 and R^4 and R^5 and R^6 in each case together form a hydrocarbon ring system of 4 to 15 carbon atoms and n is 0, 1 or 2, and

b) an open-chain or cyclic alumoxane compound of the general formula II or III



where R^7 is C_1 - C_4 -alkyl and n is from 5 to 30.

The present invention furthermore relates to a process for the preparation of polymers of propylene with the aid of these catalyst systems and to the polymers obtainable by this process.

In addition to the insoluble Ziegler-Natta catalysts, soluble catalyst systems can also be used for the polymerization of alk-1-enes. Said soluble catalyst systems are complex compounds of metals of subgroups IV and V of the Periodic Table with organic ligands, which are used in conjunction with oligomeric aluminum compounds (EP-A 185 918, EP-A 283 739 and GB-A 2 207 136). The complex compounds used in these catalyst systems contain, as organic ligands, generally cyclopentadienyl groups which

form π bonds with the transition metal. Transition metal complexes which, in addition to organic ligands, also contain halogens bonded to the metal atom are also frequently used as catalysts.

EP-A 284 708 and 316 155 and EP-A 355 447 describe soluble catalyst systems for the polymerization of alk-1-enes, in which bis(cyclopentadienyl) complexes of metals of subgroup IV of the Periodic Table are used as complex compounds, the two cyclopentadienyl rings being bonded by an alkyl-substituted silicon, tin or germanium atom or by sulfur atoms. Transition metal complexes in which the cyclopentadienyl rings are substituted by alkyl and which contain, as further ligands, two halogens bonded to the transition metal may also be used. The oligomeric aluminum compounds preferably used are linear or cyclic alumoxane compounds of the general formula II or III.

With the aid of such catalyst systems it is possible to obtain polymers of propylene which have, inter alia, a relatively narrow molecular weight distribution. In contrast to polypropylene which is prepared by using insoluble Ziegler-Natta catalysts, the molecular weights of the polypropylenes obtained in this manner are substantially lower, so that they cannot be used for many applications where polymers having molecular weights of more than 100,000 are employed.

A possible method for increasing the molecular weights of polyolefins is to reduce the reaction temperature during the polymerization. Propylene polymers having molecular weights of about 50,000 (M_w) are obtainable in this manner, for example in EP-A 355 447. In this measure, however, the increase in the molecular weights is associated with a substantial decrease in the polymerization rate, i.e. a substantial increase in the reaction time, so that the reduction of the reaction temperature has an adverse effect on the cost-efficiency of the production process.

It is an object of the present invention to overcome this disadvantage and to provide an improved soluble catalyst system which makes it possible to prepare polyalk-1-enes with high molecular weights in a very economical manner.

We have found that this object is achieved by the soluble catalyst systems defined at the outset.

According to the invention, metal complexes of the general formula I, where titanium, zirconium, hafnium, vanadium, niobium or tantalum are used as the central atom M, are used. In the metal complexes to be used according to the invention and of the general formula I, the central atom is bonded on the one hand via π bonds to substituted cyclopentadienyl groups and on the other hand to further substituents X, which may be fluorine, chlorine, bromine or iodine or C_1 - C_8 -alkyl. Metallocene complexes of the general formula I in which M is zirconium or hafnium and X is chlorine or bromine are preferably used.

Furthermore, the metal complex to be used according to the invention and of the general formula I contains, in addition to the central atom and its substituents and the substituted cyclopentadienyl groups, also a bridge member $(Z)_nY$, which bonds the two cyclopentadienyl groups to one another. Here, Y is carbon, phosphorus, sulfur, silicon or germanium, Z is C_1 - C_8 -alkyl, C_3 - C_{10} -cycloalkyl or C_8 - C_{10} -aryl and n is 0, 1 or 2.

In the preferably used metallocene complexes of the general formula I, Y is carbon, sulfur or silicon, Z is C_1 - C_4 -alkyl and n is 2.

A further important component of the metal complexes to be used according to the invention and of the general formula I are substituted cyclopentadienyl groups. These each contain radicals R^1 or R^2 which are identical or

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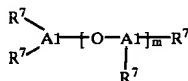
different and are each C_1 - C_4 -alkyl, in particular methyl, ethyl, isopropyl or tert-butyl. These cyclopentadienyl groups also have the substituents R^3 to R^6 , where R^3 to R^6 are identical or different and are each hydrogen or C_1 - C_8 -alkyl, or two adjacent radicals R^3 and R^4 and R^5 and R^6 in each case together form a hydrocarbon ring system of 4 to 15 carbon atoms. Metallocene complexes of the general formula I whose cyclopentadienyl groups have substituents R^3 to R^6 where R^3 and R^5 are each C_1 - C_4 -alkyl and R^4 and R^6 are each hydrogen and two adjacent radicals R^3 and R^4 and R^5 and R^6 in each case together form a hydrocarbon ring system of 4 to 12 carbon atoms, for example an indenyl system, are preferably used. The number of carbon atoms of the hydrocarbon ring systems includes the two carbon atoms of the cyclopentadienyl system which serve as linkage points with the substituents R^3 to R^6 so that, for example when R^3 and R^4 and R^5 and R^6 are in each case cyclohexyl, there are altogether two hydrocarbon ring systems, each of 6 carbon atoms.

Examples of particularly preferred metallocene complexes include

dimethylsilanediybis-(2-methylindenyl)-zirconium dichloride,
diethylsilanediybis-(2-methylindenyl)-zirconium dichloride,
dimethylsilanediybis-(2-methylindenyl)-zirconium dichloride,
dimethylsilanediybis-(2-isopropylindenyl)-zirconium dichloride,
dimethylsilanediybis-(2-tert-butylindenyl)-zirconium dichloride,
diethylsilanediybis-(2-methylindenyl)-zirconium dibromide,
dimethylthiobis-(2-methylindenyl)-zirconium dichloride,
dimethylsilanediybis-(2-methyl-5-methylcyclopentadienyl)-zirconium dichloride,
dimethylsilanediybis-(2-methyl-5-ethylcyclopentadienyl)-zirconium dichloride,
dimethylsilanediybis-(2-ethyl-5-isopropylcyclopentadienyl)-zirconium dichloride,
dimethylsilanediybis-(2-methylindanyl)-zirconium dichloride,
dimethylsilanediybis-(2-methylbenzindenyl)-zirconium dichloride and
dimethylsilanediybis-(2-methylindenyl)-hafnium dichloride.

The synthesis of such complexes can be carried out by conventional methods, the reaction of the correspondingly substituted cycloalkenyl anions with halides of titanium, zirconium, hafnium, vanadium, niobium or tantalum being preferred. Examples of corresponding preparation processes are described in, inter alia, Journal of Organometallic Chemistry 369 (1989), 359-370.

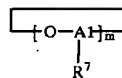
In addition to the metallocene complex, the novel catalyst system also contains linear or cyclic alumoxane compounds of the general formula II or III



(II)

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-continued



(III)

where R^7 is preferably methyl or ethyl and m is preferably from 10 to 25.

The preparation of these alumoxane compounds is usually carried out by reacting a solution of trialkyl-aluminum with water and is described in, inter alia, EP-A 284 708 and U.S. Pat. No. 4,794,096.

As a rule, the alumoxanes obtained are a form of mixtures of both linear and cyclic chain molecules of different lengths, so that m should be regarded as an average value. The alumoxane compound may also contain trialkylaluminum compounds whose alkyl groups are each of 1 to 8 carbon atoms, for example trimethyl-, triethyl- or methyldiethylaluminum.

In the polymerization of alk-1-enes with the aid of the novel catalyst system, it is advantageous to use the metallocene complex a) and the alumoxane compound b) in amounts such that the atomic ratio of aluminum from the alumoxane b) to the transition metal from the metallocene complex a) is from 10:1 to 10⁶:1, in particular from 10:1 to 10⁴:1. The two catalyst components can be introduced into the polymerization reactor individually in any order or as a mixture. A particularly reactive soluble catalyst system is obtainable when the metallocene complex a) and the alumoxane compound b) are mixed with one another from 5 to 60, preferably from 10 to 40, minutes before the actual polymerization. The catalyst activated in this manner can then be used immediately.

With the aid of these soluble catalyst systems, it is possible to prepare polymers of alk-1-enes. These are understood as meaning homo- and copolymers of C_2 - C_{10} -alk-1-enes, ethylene, propylene, but-1-ene, pent-1-ene and hex-1-ene preferably being used as monomers. The novel catalyst systems are particularly suitable for the preparation of polypropylene and of copolymers of propylene with minor amounts of other C_2 - C_{10} -alk-1-enes, in particular of ethylene and but-1-ene.

The preparation of these polymers can be carried out in the conventional reactors used for the polymerization of alk-1-enes, either batchwise or, preferably, continuously. Suitable reactors include continuously operated stirred kettles and a number of stirred kettles connected in series may also be used.

The polymerization is carried out at from 0.1 to 3,000, preferably from 0.5 to 2,500, bar and from -20 to 300° C., preferably from +10 to +150° C. The polymerization time is usually from 0.5 to 10 hours.

Polymerization reactions carried out with the aid of the novel catalyst system can be effected in the gas phase, in liquid monomers or in inert solvents. The polymerization in solvents, in particular in liquid hydrocarbons, such as benzene or toluene, is preferably used. In this case, it is advantageous if from 10⁻⁴ to 10⁻¹ mol of aluminum as alumoxane is used per liter of the solvent.

The average molecular weight of the polymers formed can be controlled by the methods conventionally used in polymerization technology, for example by the addition of regulators, such as hydrogen, or by changing the reaction temperatures.

Polymers prepared with the aid of the novel catalyst systems have a high molecular weight and a narrow molecu-

lar weight distribution. They can also be prepared at relatively high temperatures, with the result that the polymerization time can be limited. Owing to these properties, the polymers obtainable using the novel catalyst systems are particularly suitable for the production of films and moldings.

EXAMPLES FOR THE PREPARATION OF POLYPROPYLENE

Example 1

350 ml of dry toluene were initially taken in a stirred autoclave having a useful volume of 1 l, and a solution of 0.45 g of methylalumoxane (average chain length $m=20$) in 30 ml of toluene was then added. $7.6 \cdot 10^{-3}$ mol of aluminum was used per liter of the solvent. A solution of 15 mg of dimethylsilanediybis-(2-methylindenyl)-zirconium dichloride (corresponding to $31.2 \cdot 10^{-6}$ mol) in 15 ml of toluene was then added, so that the atomic ratio of aluminum to zirconium was 244:1. This mixture was first stirred for 30 minutes at 50°C ., after which propylene was forced in under a pressure of 2 bar and polymerization was carried out for 4 hours and 40 minutes. The polymerization was effected at 50°C . and 2 bar. Thereafter, unconsumed propylene was removed and a mixture of 1 l of methanol and 10 ml of concentrated hydrochloric acid were added to the reaction solution. The precipitated polymer was filtered off, washed with methanol and dried under reduced pressure. 45 g of polypropylene having a weight average molecular weight (\overline{M}_w) of 114,200, a number average molecular weight (\overline{M}_n) of 41,500 and a molecular weight distribution ($\overline{M}_w/\overline{M}_n$) of 2.75 were obtained.

Example 2

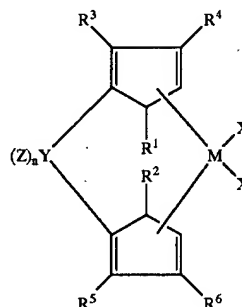
The procedure was similar to that of Example 1, 350 ml of dry toluene likewise being initially taken and a solution of 0.45 g of methylalumoxane ($m=20$) in 30 ml of toluene then being added. Thereafter, a suspension of 0.5 mg of dimethylsilanediybis-[3,3'-(2-methylbenz-indenyl)]-zirconium dichloride in 20 ml of toluene was added, so that the atomic ratio of aluminum to zirconium was 8950:1. The further procedure was then as described under Example 1.

51.4 g of polypropylene having a weight average molecular weight (\overline{M}_w) of 142,896, a number average molecular weight (\overline{M}_n) of 91,917 and a molecular weight distribution of 1.55 were obtained.

Pentad content, measured by ^{13}C -NMR: amount mmmm=93.5%.

We claim:

1. A metallocene complex of the formula I



where M is titanium, zirconium, hafnium, vanadium, niobium or tantalum, X is halogen or $\text{C}_1\text{--C}_8$ -alkyl, Y is carbon, phosphorus, sulfur, silicon or germanium, Z is $\text{C}_1\text{--C}_8$ -alkyl, $\text{C}_3\text{--C}_{10}$ -cycloalkyl or $\text{C}_6\text{--C}_{10}$ -aryl, R^1 and R^2 are identical or different and are each $\text{C}_1\text{--C}_4$ -alkyl, two adjacent radicals R^3 and R^4 and R^5 and R^6 in each case together form a hydrocarbon ring system of 10 to 15 carbon atoms and n is 0, 1 or 2.

2. A metallocene complex as claimed in claim 1, in which M is hafnium or zirconium.

3. A metallocene complex as claimed in claim 1, in which X is chlorine or bromine.

4. A metallocene complex as claimed in claim 1, in which Y is carbon, sulfur or silicon.

5. A metallocene complex as claimed in claim 1, wherein R^1 and R^2 are identical or different and are each methyl, ethyl, isopropyl or tert-butyl.

6. A metallocene complex as claimed in claim 1, in which two adjacent radicals R^3 and R^4 and R^5 and R^6 in each case together form a hydrocarbon ring system of 10 to 12 carbon atoms.

7. Dimethylsilanediybis-(2-methylbenzindenyl)-zirconium dichloride.

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